

Analysis of persistent organic pollutants in marine sediments using a novel microwave assisted solvent extraction and liquid-phase microextraction technique

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Abstract

A simple and novel analytical method for quantifying persistent organic pollutants (POPs) in marine sediments has been developed using microwave assisted solvent extraction (MASE) and liquid-phase microextraction (LPME) using hollow fibre membrane (HFM). POPs studied included twelve organochlorine pesticides (OCP) and eight polychlorinated biphenyl (PCB) congeners. MASE was used for the extraction of POPs from 1 g of sediment using 10 ml of ultrapure water at 600 W for 20 min at 80 °C. The extract was subsequently subjected to a single step LPME–HFM cleanup and enrichment procedure. Recovery varied between 73 and 111% for OCPs; and 86–110% for PCBs, and exceeded levels achieved for conventional multi-step Soxhlet extraction coupled with solid-phase extraction. The method detection limit for each POP analyte ranged from 0.07 to 0.70 ng g⁻¹, and peak areas were proportional to analyte concentrations in the range of 5–500 ng g⁻¹. Relative standard deviations of less than 20% was obtained, based on triplicate sample analysis. The optimized technique was successfully applied to POP analysis of marine sediments collected from the northeastern and southwestern areas of Singapore's coastal environment.

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1. Introduction

There is growing evidence that xenobiotic chemicals in the environment have the potential to elicit endocrine disruption in biota by impacting upon reproductive and hormonal functions [1]. Although these effects are not restricted to persistent organic pollutants (POPs) alone, these compounds are an important component of the range of xenobiotic chemicals now ubiquitous in the global environment [2–4]. Chlorinated organic compounds have a wide range of industrial and agricultural applications, and include organochlorine pesticides (OCPs), such as dichlorodiphenyltrichloroethane (DDT) and Lindane (γ -HCH; hexachlorocyclohexane (HCH)), as well as the polychlorinated biphenyls (PCBs). Moreover, these compounds are chemically and biologically

recalcitrant and readily undergo bioaccumulation in both terrestrial and aquatic organisms [5,6]. Introduction of these compounds into the marine environment via atmospheric deposition, oil spillages and sewage discharges results in their biomagnification in the food chain, ultimately posing a risk to human health [7]. Indeed, POPs are now routinely detected in fish and wildlife, as well as human adipose tissue, blood and breast milk [8,9].

The quantification of POPs in marine sediments can be achieved via several established methods. For example, USEPA method 3540 (Soxhlet extraction) has been used for extracting semi-volatile organic pollutants from sediments, as well as soils and solid wastes. In recent years, new extraction procedures have been developed for POPs in sediment samples. Supercritical fluid extraction (SFE), accelerated solvent extraction (ASE) [10–12] and microwave assisted solvent extraction (MASE) [13,14] have all have been used. These techniques have allowed sample size and solvent

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volume to be reduced, analytical precision to be improved. The main advantage of MASE is that it provides faster and more efficient sample extraction due to direct heat transfer by ionic conduction and dipole rotation.

Non-polar solvents do not absorb microwave energy. Therefore, in MASE, such solvents have poor extraction efficiencies compared to polar solvents or mixtures of solvents at least one of which must polar [15]. Addition of water (which is polar) improves the recoveries of the target analytes [16] as it facilitates non-polar organic solvents to absorb the microwave energy, and also enhances the release of analytes from the sample matrix [17]. Recently, water has been used as an alternative solvent as it is cost effective, safe and environmentally benign. As water has a higher permittivity (ϵ) and heat of vaporization (ΔH_v (kJ mol⁻¹), (78.3 and 46.0 at 25 °C) compared to organic solvents such as acetone (20.7 and 31.9 at 25 °C), hexane:acetone mixtures (1.9 and 31.9 at 20 °C) and methanol (32.6 and 37.5 at 20 °C), respectively [18], it is suitable for many polar analytes and has a better extraction efficiency than organic solvents during microwave extraction [19]. Moreover, after MASE with solvent, a clean-up step is required due to co-extraction of matrix materials with the solvent, thereby resulting in interferences during chromatographic separation [20,21].

Various types of solid phase extraction (SPE) cartridges have been used for sample clean up which includes C18, silica or ion exchange materials [22–24] that depend upon moderate to large amounts of solvent. Solid phase microextraction (SPME), a solventless extraction technique coupled to MASE has also been developed, although it is not widely deployed (in most cases, microwave digested samples were extracted using HS-SPME, and this reduces the sensitivity for semi- or nonvolatile analytes) as the fibers used are prohibitively expensive and subject to analyte carryover [25].

To overcome these shortcomings, we have developed a simple liquid-phase microextraction (LPME) cleanup and enrichment procedure supported by porous polypropylene hollow fiber membrane (HFM). HFM has already been shown to be effective for the enrichment and cleanup of various analytes in different media [26], including water, slurry [27], human urine, and plasma [28–30]. Recently, LPME has been successfully applied to soil samples by direct immersion-LPME [31] and headspace-LPME [32]. In this study we develop a MASE procedure coupled with LPME using HFM for cleanup, enrichment and extraction of POPs (i.e. OCPs and PCBs) from marine sediment samples. The new method was then applied to the analysis of POPs in marine sediments collected from Singapore's coastal marine environment.

2. Experimental section

2.1. Standard and reagents

HPLC grade solvents were purchased from Merck (Darmstadt, Germany). Ultrapure water was obtained from a Milli-Q system (Millipore, Milford, MA, USA). All pesticides used

were purchased from Poly Science (Niles, IL, USA). A mixed stock solution containing twelve OCPs (i.e. α -HCH, β -HCH, Lindane, Heptachlor, Aldrin, Dieldrin, Endrin, Endosulfan, *p,p'*-dichlorodiphenyldichloroethane (*p,p'*-DDD), *p,p'*-DDT, Endrin aldehyde and Methoxychlor) and eight PCB congeners (i.e. 2-dichlorobiphenyl (CB-1), 2,3-dichlorobiphenyl (CB-5), 2,4,5-trichlorobiphenyl (CB-29), 2,2',4,4'-tetrachlorobiphenyl (CB-47), 2,2',3',4,6-pentachlorobiphenyl (CB-98), 2,2',4,4',5,6'-hexachlorobiphenyl (CB-154), 2,2',3,3',4,4',6-heptachlorobiphenyl (CB-171), 2,2',3,3',4,5',6,6'-octachlorobiphenyl (CB-200)) were obtained from Aldrich (Milwaukee, WI, USA).

A working standard solution of 1 $\mu\text{g ml}^{-1}$ per OCP or PCB analyte was prepared by stock dilution in acetone. Oasis-HLB SPE cartridges were purchased from Waters (Milford, MA, USA). A MARS (CEM, Matthews, NC, USA) microwave extraction system (maximum power: 1200 W) was used for POP extraction from sediment. Accurel Q3/2 polypropylene HFM was purchased from Membrana GmbH (Wuppertal, Germany) and used in conjunction with a 10 μl micro syringe (needle tip 0.46 mm O.D.) purchased from Hamilton, Reno, NV, USA. The inner diameter of the HFM was 600 μm , wall thickness 200 μm and pore size 0.2 μm .

2.2. Sediment preparation

Solvent-washed blank sediment sample (pH 6 and total organic content 1.8%) was prepared using our previous procedure [33] and tested for POP analysis using Soxhlet extraction and no target analytes were detected. Several of the sediment samples were prepared by spiking appropriate amounts of the diluted working standards solutions to get final concentrations of 5–500 ng g⁻¹ sediment. The sediments were first homogenized by hand mixing for ~2 min and afterwards in a mechanical shaker while they were left for at least 4 h at room temperature to fully evaporate the solvent. Real sediment sampling was conducted from three locations in the northeastern and southwestern regions of Singapore's coastal environment. Sampling locations were all within 1 km of the busy industrial and shipping lane of the coastline. Surface sediments were collected using a Van Veen grab (1000 cm² sampling area). The samples were first air dried to constant mass at room temperature and then sieved through a screen (pore size 2 mm I.D.) to remove rocks, coarse particles and other large debris. A portion of the sediments were analysed using Soxhlet extraction prior to spiking. The pH value and organic content of the sediments were 8.2 and 4.6%, respectively.

2.3. MASE–LPME–HFM extraction

A 1 g sample of sediment was subjected to microwave heating with 8 ml of ultrapure water at 600 W. Water was the solvent used for MASE as it has high dielectric constant (i.e. 78.3 ϵ), dipole moment, (i.e. 2.3), dissipation factor, (i.e. 1570 $\tan \delta \times 10^{-4}$) and boiling point compared to

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